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ELECTROCALORIC REFRIGERATION FOR SUPERCONDUCTORS

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SEMI-ANNUAL TECHNICAL REPORT
ELECTROCALORIC REFRIGERATION FOR SUPERCONDUCTORS

ARPA Order 2535; NBS CC# 2750489
for the period ending December 31, 1974

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SUMMARY
OF
SEMI-ANNUAL TECHNICAL REPORT
ELECTROCALORIC REFRIGERATION FOR SUPERCONDUCTORS

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Several significant developments have occurred in the six month period since the previous Semi-Annual Technical Report. The most significant development was the discovery that SrTiO_3 glass ceramics (FEL multilayer samples) showed only heating effects at 4K for both polarization and depolarization. At the same time, the pitting problem for ceramming temperatures above 1100°C was partially solved. The ceram temperature at which large pits now first appear has been increased to 1160°C . Those samples showed some improvement in dielectric properties but they still showed only heating effects at 4K.

Development work on two types of heat switches was essentially completed. The gold-plated multiple leaf heat switch was shown to be useful for heat loads up to about 1 watt at 4K. The magnetothermal conductivity measurements on single crystal beryllium indicate that it could be used for both the upper and lower switch. A few details on the magnetothermal switches remains to be done as well as a test of the helium gap heat switch. This further work has been temporarily suspended in order to concentrate fully on solving the refrigerant material problem.

Several electrothermal measurements have been done on the SrTiO_3 glass-ceramic samples to try to understand why they behave as they do. In addition an apparatus for measurement of DC polarization and hysteresis was completed. The results from those measurements are consistent with the electrothermal measurements. A phenomenological understanding of the problem has resulted from these measurements, but there are still several points which are not understood in detail. Studies of several new materials have begun in order to better understand the electrocaloric effect near 4K and in hopes of finding a satisfactory refrigerant material.

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1. INTRODUCTION

To review briefly, SrTiO_3 glass-ceramics were developed which displayed a dielectric constant (ϵ) peak at about 33K and $d\epsilon/dT$ at 4K ranges up to 25K^{-1} (in research samples). Polarization-field measurements by the a.c. bridge method showed that for field strengths up to 205 kV/cm, the hysteresis loop was very slim and the residual polarization very small, indicating a paraelectric \rightarrow antiferroelectric phase transition in the SrTiO_3 crystallites at 33K (x-ray data show that the dielectric anomaly is associated with a cubic \rightarrow tetragonal structural change in the SrTiO_3 crystals). These properties suggested the material could be used as a refrigerator, since $(\partial S/\partial E)_T = (\partial P/\partial T)_E \propto (\partial \epsilon/\partial T)_E > 0$.

Multilayer SrTiO_3 glass-ceramic samples fabricated in Rayleigh have been plagued by pitting for ceram temperatures above 1100°C . Consequently, considerable effort was devoted to optimizing the 1100°C process conditions. Most of the work discussed in this report are on FEL samples cerammed at 1100°C under optimum conditions up to 1/1/75. A. J. Morrow has quite recently solved the pitting problem to some extent. Now samples can be cerammed at temperatures up to 1160°C before severe pitting occurs. Some results on these samples are also discussed in this report. The most significant development was the finding that all of the FEL multilayer samples showed only heating effects at 4K for both polarization and depolarization.

2. HEAT SWITCHES

Development work on two types of heat switches was essentially completed. The gold-plated multiple leaf switch was shown to be useful for heat loads up to about a maximum of 1 watt at 4K or 4 watts at 16K. Higher heat loads require so many leaves (≥ 5) that it is difficult to separate them in the "off" case. The resulting "on" to "off" ratio is then too low to be a useful heat switch.

Results of the magnetothermal conductivity measurements on single crystal beryllium, shown in Fig. 1, indicate that it could be used for both the upper and lower switch, although an actual Be switch has not yet been demonstrated. Measurement of the thermal boundary resistance across a solder joint between beryllium and copper has yet to be measured. Tests of the helium gap switch have been postponed so that our full effort can be concentrated on the refrigerant material.

3. ELECTROTHERMAL MEASUREMENTS ON FEL MULTILAYER SAMPLES

3.1 Experimental Techniques

The previous technical report gave details of the apparatus in which specific heat, electrocaloric effect and dielectric constant can be measured on two samples, and an NBS Tech. Note has been prepared. A very brief description is given here for completeness. Each sample is mechanically supported in vacuum from a thermal reservoir by a carbon radio resistor. This resistor also acts as the thermal link between the sample and the reservoir with a resulting thermal time constant that usually varies between about 1 minute at 2K to about 10 minutes at 20K. Heat pulses can be applied to the sample by a resistance wire varnished on one side of the sample and insulated from the sample electrodes. High voltage lead connected to the sample electrodes permit large electric fields to be applied to the sample. A carbon thermometer varnished on the sample detects the temperature change when either a heat pulse is applied (specific heat) or a change in electric is applied (electrocaloric effect). A capacitance bridge is used to measure the dielectric constant of the sample.

3.2 Effects of Initial Polarization

The first observation was that the initial voltage application at 4K caused heating rather than the expected cooling. Moreover, this heating persisted for very long times. Data are shown in Fig. 2 for two FEL samples cerammed at 1100°C where at $t = 0$ the field was switched $0 \rightarrow 239$ kV/cm. These data were obtained by analyzing $T(t)$ data knowing thermal conductance data $G(T)$ for the thermal links. For times ~ 40 min., the heating has fast and slow components with time constant ~ 2 min. and ~ 20 min., respectively. Considerable energy is dissipated in this process, $\sim 0.1 - 0.2$ J/cm³ from Fig. 2. It was found experimentally that once these initial mechanisms stabilized at some field value, the field could then be reduced, cycled, etc. without re-triggering these mechanisms. Qualitatively the same results were seen in FEL samples cerammed at temperatures between 1000°C and 1160°C. Samples prepared at 915°C came into equilibrium almost immediately (i.e., at 915°C no significant crystallization has occurred).

3.3 Electrocaloric Effect in Stabilized Samples

The large heating observed during the initial polarization of the sample is not important for a refrigerator. The important thing is what happens during subsequent polarization and depolarization cycles with the electric field always in the same direction as that used to initially polarize the sample. Such polarization and depolarization measurements were done on several FEL samples with different ceram temperatures. All samples behaved qualitatively the same. For temperatures between 2 and 7K only heating effects were seen as shown in Fig. 3 for two FEL

samples cerammed at 1100°C . Values for ΔT are about the same for both polarization and depolarization and are quantitatively consistent with hysteresis heating that was calculated from measurements of the hysteresis loop. This heating is much smaller than the expected cooling effects during polarization. Below 4K there is essentially no difference in the ΔT for polarization compared with depolarization. Above 4K there does appear to be some difference. Such a difference indicates there is a small reversible cooling effect during depolarization and a small reversible heating effect during polarization that is superimposed on the hysteretic heating.

Figure 4 shows the ΔT behavior of the same samples in the temperature range 20-40K. At this temperature the reversible electrocaloric heating and cooling effects dominate the hysteretic heating. The deviation of the points from the curve at the lower temperatures would be a result of the small hysteretic heating. Samples cerammed at other temperatures show similar behavior although there is a general trend toward a larger electrocaloric effect for higher ceram temperatures.

3.4 Specific Heat

The zero field specific heat of an unelectroded FEP sample cerammed at 1100°C is shown in Fig. 5. The FEL samples should have a similar behavior. This figure also shows the specific heat of a glass, fused SiO_2 , and the specific heat of a single crystal SrTiO_3 . The single crystal SrTiO_3 specific heat curve is from unpublished data by J. H. Colwell of NBS, Washington. The FEP glass-ceramic is approximately 50% SrTiO_3 and 50% glass phase, though the glass phase is an aluminosilicate rather than fused SiO_2 . The specific heat of the FEP glass-ceramic appears consistent with what would be expected of a mixture of SrTiO_3 and glass. The data show no indication of a large anomaly in the range 3-20K. A transition from an antiferroelectric state (or ferroelectric state) to a paraelectric state would give rise to a peak in the specific heat at the transition temperature. Such peaks are usually spread out somewhat in temperature, but the specific heat of FEP and 20K shows no apparent indication of any approaching peak at 33-40K. The possibility of a sharp peak at 33-40K cannot be ruled out until zero field specific heat data are obtained in that temperature range.

The specific heats of the two FEL samples used in the electrocaloric effect experiments were measured at 4.4K as a function of electric field. For an electric field of 220 kV/cm the specific heat decreased only about 5% compared with the zero field specific heat. Thus the change in entropy at 4K with electric field is also very small.

4. D.C. POLARIZATION MEASUREMENTS ON FEL MULTILAYER SAMPLES

The change in entropy with electric field is given by the Maxwell relation,

$$\left(\frac{\partial S}{\partial E}\right)_T = \left(\frac{\partial P}{\partial T}\right)_E, \quad (1)$$

where P is the polarization of the sample and E is the applied electric field. If P shows no hysteresis effects upon cycling E , then P can be determined from the expression

$$P(E) = \int_0^E \epsilon(E) dE, \quad (2)$$

where $\epsilon(E)$ is the A.C. dielectric constant measured as a function of D.C. bias field. This expression was used for all of the previous calculations. If significant hysteresis is present, Eq. (2) is no longer valid and P then must be measured directly with a circuit like that described below.

4.1 Experimental Techniques

Hysteresis curves on a dielectric are usually produced with a Sawyer-Tower circuit operating at 50-60 Hz. In such a circuit, the polarization of the dielectric sample is proportional to the voltage developed across a large standard capacitor in series with the capacitor containing the dielectric sample. This voltage is applied to the vertical deflection of an oscilloscope or an x-y recorder, and the voltage across the sample capacitor is fed to the horizontal deflection. A high voltage oscillator drives the circuit. Because of the long equilibrium times encountered during the initial polarization of the FEL glass ceramics, it was important to reduce the oscillation frequency in such a circuit to the point where a single cycle would require several hours to complete.

It was desired to have a circuit that, in addition to measuring hysteresis curves, could also measure the temperature dependence of polarization in a constant field. Consequently the required circuit had to be a quasi-D.C. one in which the hysteresis curves are mapped out point-by-point. In that case, the voltage across the standard capacitor must be measured with an electrometer. Its input impedance is so high that the time constant for voltage decay on the standard capacitor is on the order of days. A digital voltmeter was connected to the output of the electrometer to obtain better resolution. The internal resistance of the sample capacitor must also be high enough ($R \geq 10^{12}\Omega$) to make

leakage currents negligible during the measurements. A high voltage D.C. power supply was connected across the standard and sample capacitors in series. Because the capacitance of the standard is much larger than that of the sample, the voltage applied to the sample is essentially that of the power supply. It can be shown that in a circuit like that just described the electric displacement D in the sample is given by

$$D = C_S V_S / A, \quad (3)$$

where C_S is the capacitance of the low leakage standard capacitor, V_S is the voltage across the standard capacitor, and A is the electrode area of the sample capacitor. All the materials being studied in this program have relative dielectric constants much larger than one. Hence the polarization is then simply $P = D = C_S V_S / A$.

4.2 Initial Polarization

Initial polarization of the FEL glass-ceramic samples gave rise to large heating effects (Section 3.2) with decay time constants of several minutes. The only exception was a sample prepared at 915°C. The modified Sawyer-Tower circuit described above was used to measure the time dependence of the polarization in several FEL samples when a field was first applied to the sample at a temperature of 4K. Samples warmed to room temperature appear to lose all memory of previous polarizations at 4K. Figure 6 shows how the initial polarization at 4K changes with time in a FEL sample cerammed at 1090°C. Curves are shown for two different field values. The initial polarization increases with time and finally approaches an equilibrium value $P(\infty)$ after a few hours. The time constants are comparable to that seen in the heating effects in Fig. 2, but a single time constant cannot be used to fit the data.

4.3 Hysteresis Loops

Figure 7 shows a typical hysteresis curve on the FEL samples. The curve shown is taken at 4K on a sample cerammed at 1090°C. About an hour was taken to complete the cycle. Note that hysteresis is considerably reduced for a cycle in only one direction of the applied field, provided the maximum field does not exceed that of the initial polarization in the same direction. The value of P for $E = 0$ is called the remanent polarization, P_r . The total polarization can then be written as a sum of two parts,

$$P = P_E + P_r \quad (4)$$

where P_E is that part of the polarization induced by the electric field. Actually P_r is dependent on the maximum field applied, but for fields on the order of 300 kV/cm the sample is nearly saturated and P_r increases very little with increasing field. The A. C. dielectric constant measurements determine essentially just P_E via Eq. (2). The rather large values of P_r were not expected and are indicative of ferroelectric behavior rather than the expected antiferroelectric behavior. Additional explanations of these effects are given in section 5.

4.4 Temperature Dependence of Polarization

As shown by Eq. (1), the temperature dependence of P determines the entropy change for a given field change. Figure 8 shows results of measurements of P as a function of temperature on several FEL samples which had different ceramic temperatures. The P curves were measured with a field of 3.54 kV/cm applied as the samples were cooled from 77K. The P curves were measured after the field was taken off at 4K and as the samples were warmed up. These curves are actually somewhat history dependent, as would be expected in samples which show hysteresis. The P_E curves shown in Fig. 8 are merely the difference between P and P_r . The P_E curves show a behavior similar to that of the dielectric constant measured by an A. C. capacitance bridge. It should be emphasized that Fig. 8 shows the normalized polarization P/P_0 , P_E/P_0 , and P_r/P_0 , where P_0 is the value of P at 0 K. Values of P_0 for the different ceramic temperatures are: 915°C, 0.0082 $\mu\text{C}/\text{cm}^2$; 1000°C, 0.0655 $\mu\text{C}/\text{cm}^2$; 1090°C, 0.169 $\mu\text{C}/\text{cm}^2$; 1160°C, 0.167 $\mu\text{C}/\text{cm}^2$.

The important thermodynamic quantity is P , which shows no temperature dependence below about 10-15K. The observation of electrocaloric effects in the 20-40K temperature range but not at 4K is thus consistent with the polarization measurements.

5. DISCUSSION

We now understand the behavior of the FEL glass ceramics from a phenomenological standpoint. From a microscopic standpoint, there are several things not understood yet. The hysteresis effects are indicative of a ferroelectric material. It is not too surprising that at 4K equilibrium times for domain reversal can be on the order of hours for the field strengths used. What is surprising is the fact that the remanent polarization persists even for temperatures greater than 77K. It is known from x-ray data that the SrTiO_3 crystals, in the glass-ceramic are cubic for temperatures of 77K and above. Thus they should not show a remanent polarization from symmetry considerations. The observation of an apparent remanent polarization could be explained in several ways: (1) the remanent

polarization exists only in the glass phase, (2) application of a field destroys the cubic symmetry, or (3) the apparent remanent polarization is actually due to the injection and storage of charges near the surface next to the electrodes. This third possibility is not a true polarization but it is commonly observed in electrets. The recent observation of an apparent polarization in a pure cubic single crystal of KTaO_3 could tend to rule out point (1). Measurements on other SrTiO_3 glass-ceramics with different glass compositions are planned to check point (1) further.

The measured electrocaloric effects in the FEL samples are in quantitative agreement with the temperature dependence of the total polarization. Though there is a general trend of an increased electrocaloric effect for higher ceramic temperatures, the increase is not very rapid. We conclude that the FEL glass-ceramics cannot be used for refrigeration below 15K. Experiments are now underway to determine if a different glass composition or the elimination of the 2% Nb_2O_5 content in the SrTiO_3 will increase the electrocaloric effect.

6. FUTURE WORK

The materials aspect of the program has been expanded to test several other candidate cooling materials. The most promising material to date is a single crystal of KTaO_3 obtained from Sandia. Attempts to make KTaO_3 into a glass-ceramic and a ceramic are underway by A. J. Morrow at Raleigh.

Other samples to be tested are various lead zirconate-titanate (PZT) compositions. These have antiferroelectric or ferroelectric transitions somewhat above room temperature but show a temperature dependence in the dielectric constant at 4K. The entropy change at the transitions are larger than required. Whether enough of this entropy is left at 4K to do any significant refrigeration is still uncertain, but it appears doubtful from thermodynamic considerations.

Lead niobate and some of its relatives have transitions to the antiferroelectric state in the range of 15-50K. Thus most of the polar entropy is available for cooling in the 15-4K range. Whether there is enough entropy at the transition is a question that needs to be answered. Preparation of lead niobate samples is in progress by A. J. Morrow.

7. FIGURE CAPTIONS

- Figure 1. Thermal conductivity versus temperature for a single crystal of beryllium in various transverse magnetic fields. The heat flow is parallel to the c axis and the magnetic field parallel to the a axis. This sample had a residual resistance ratio (RRR) of 1500. The data of Gruneisen and Adenstedt [Ann. d. Phys. [5] 31, 714 (1938)] is shown for comparison.
- Figure 2. The time dependence of self heating in two FEL glass-ceramic after an electric field is first applied to the samples at 4K. Both samples had ceramic temperatures of 1100°C.
- Figure 3. The temperature rise in two previously polarized FEL samples during a change in the electric field. The open symbols are for an increase in field and the closed symbols are for a decrease in field.
- Figure 4. The temperature change in two previously polarized FEL samples during a change in the electric field. This data is for the 20-40K temperature range where cooling is seen for a decrease in field.
- Figure 5. The specific heat of FEL glass-ceramic in zero applied electric field. Shown for comparison are specific heat curves for fused SiO_2 and single crystal SrTiO_3 .
- Figure 6. The time dependence of the polarization after an electric field is first applied to a FEL sample at 4K. The relative change, $[P(\infty) - P(t)]/P(\infty)$ is actually shown, where $P(t)$ is the polarization at the time t and $P(\infty)$ is the equilibrium value that is reached after a long time.
- Figure 7. The polarization hysteresis curves at $T = 4\text{K}$ for a FEL sample cerammed at 1090°C. The larger loop occurs when the field is cycled between -56 kV/cm and +56 kV/cm. The remanent polarization is indicated by P_r . The smaller loop occurs when the field is cycled between 0 and +56 kV/cm.
- Figure 8. The temperature dependence of the normalized polarization for FEL samples cerammed at different temperatures. The normalization constant P_0 is the extrapolated value of the total polarization, P , at 0 K. The remanent polarization, P_r , and the field induced polarization, P_E , are also normalized by P_0 .

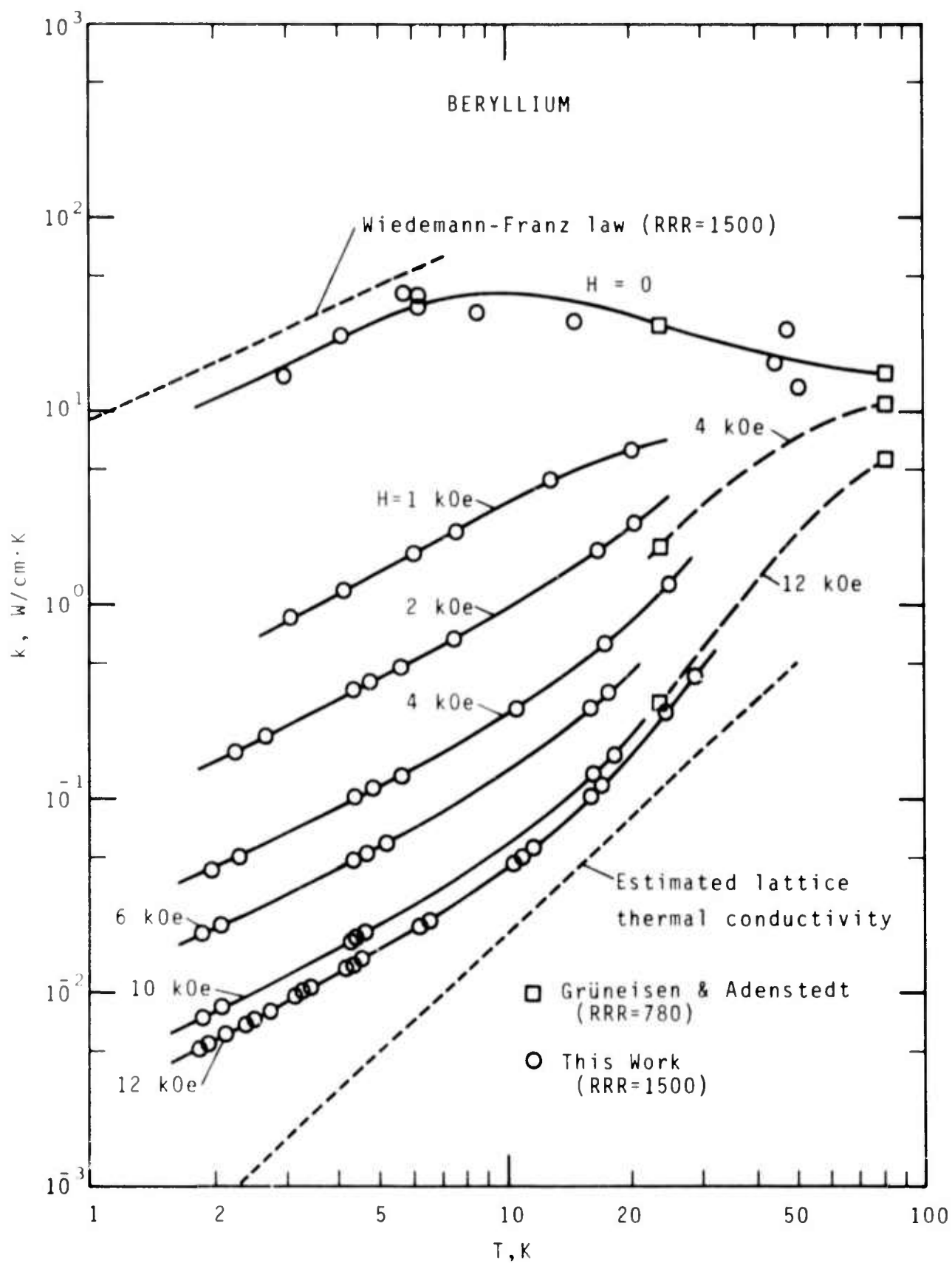


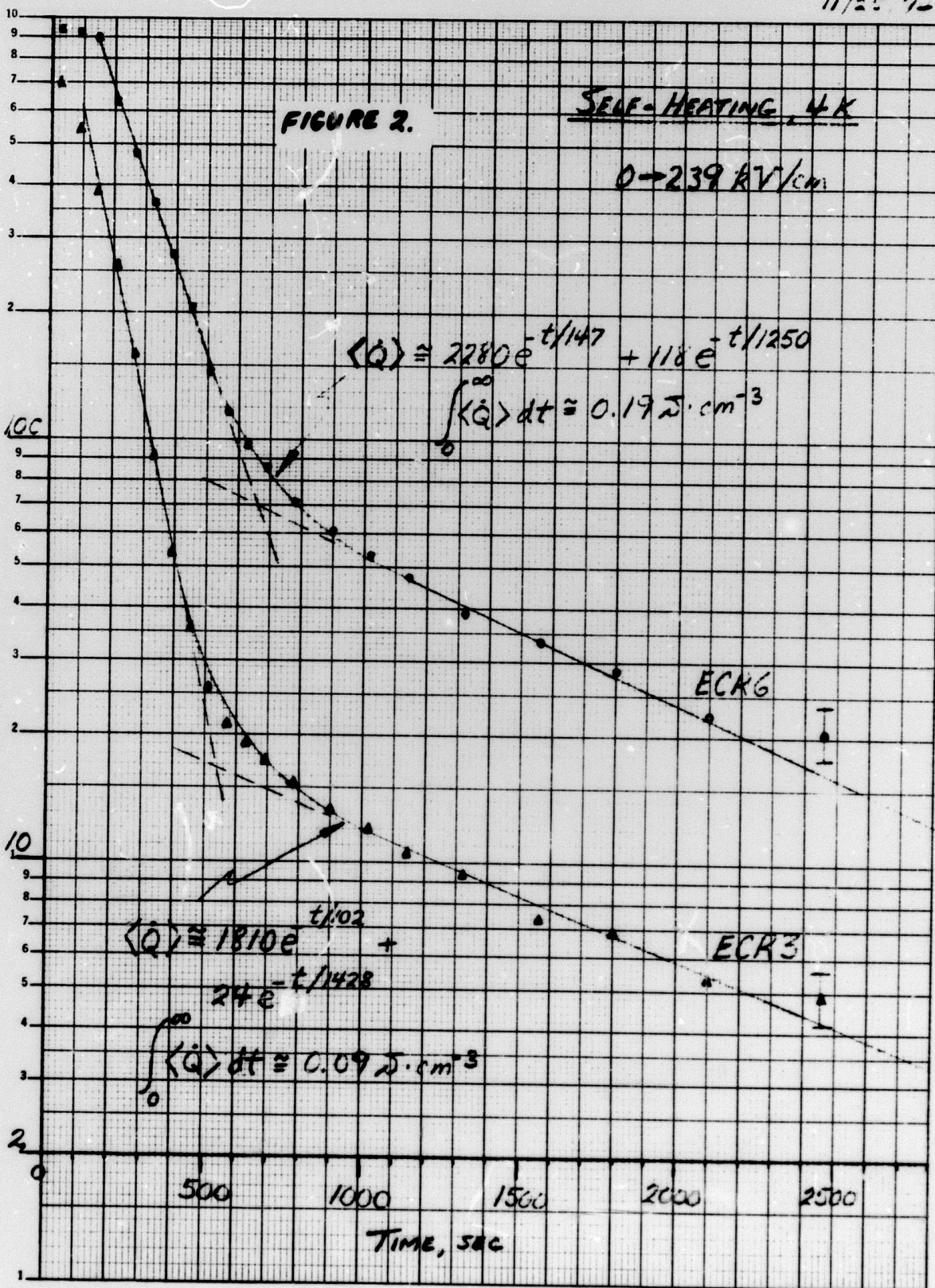
FIGURE 1

WAL
11/25/70

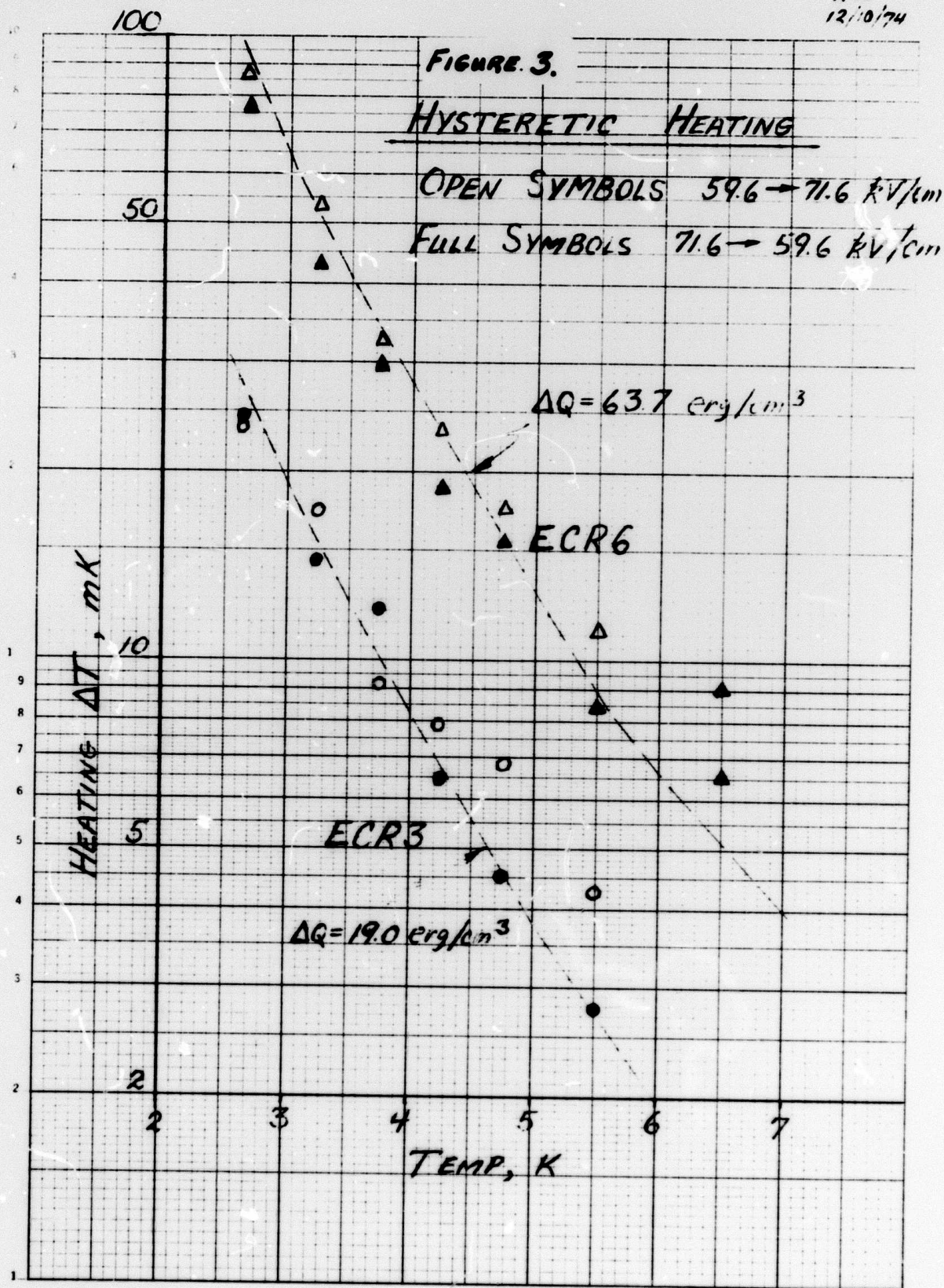
FIGURE 2.

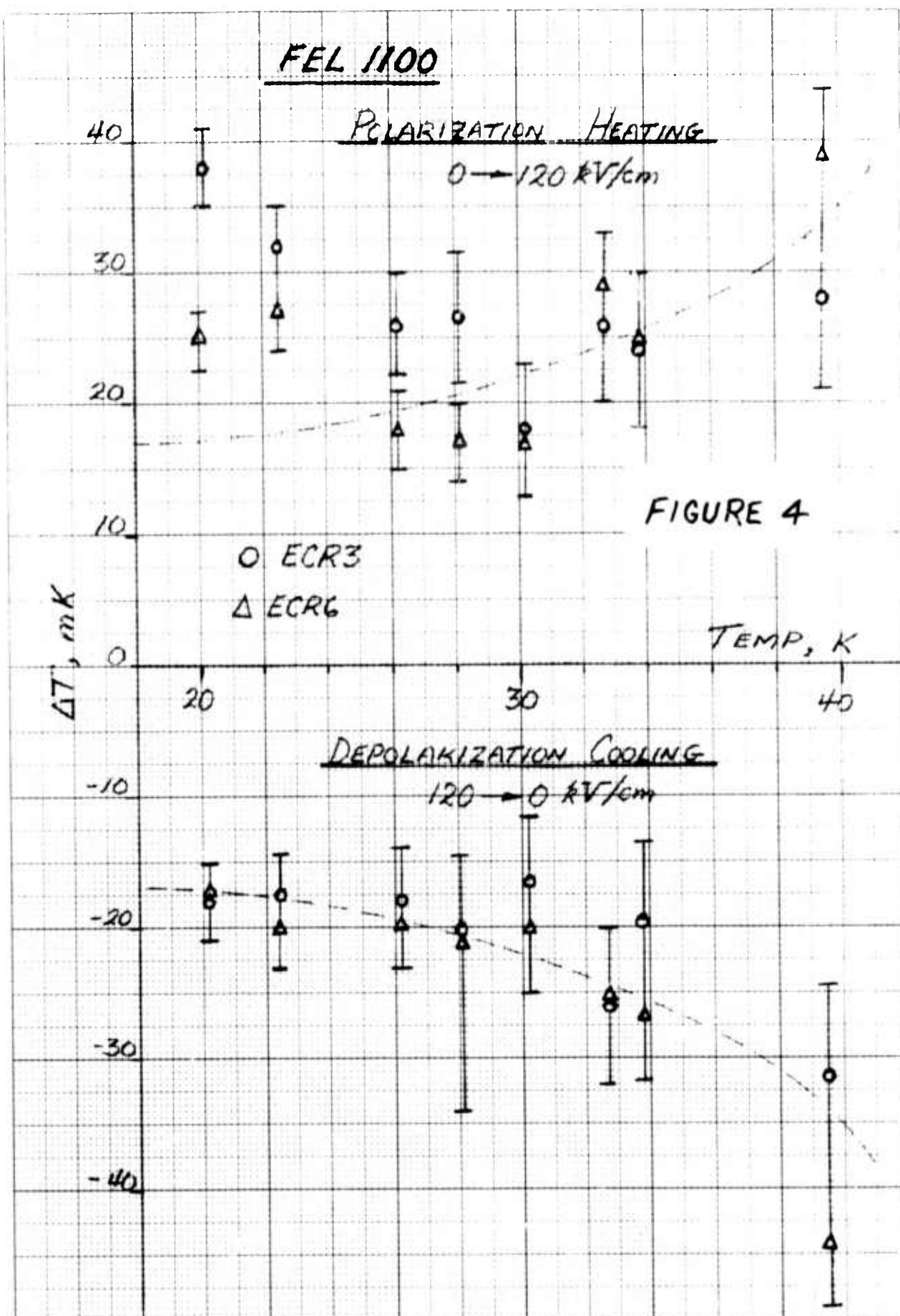
SELF-HEATING, 4 K

$0 \rightarrow 239 \text{ kV/cm}$



WAL
12/10/74





$C_0, \text{erg} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$

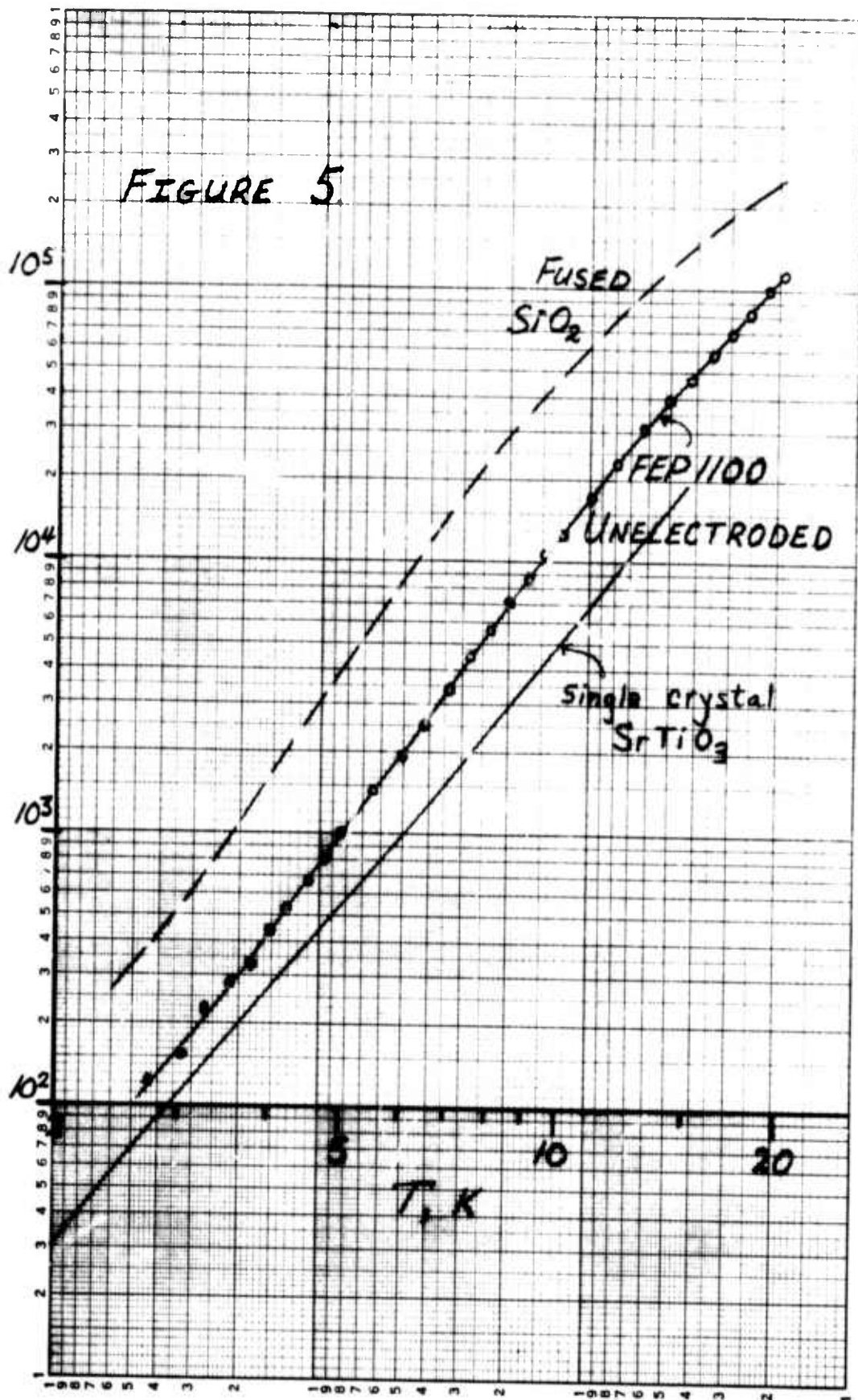
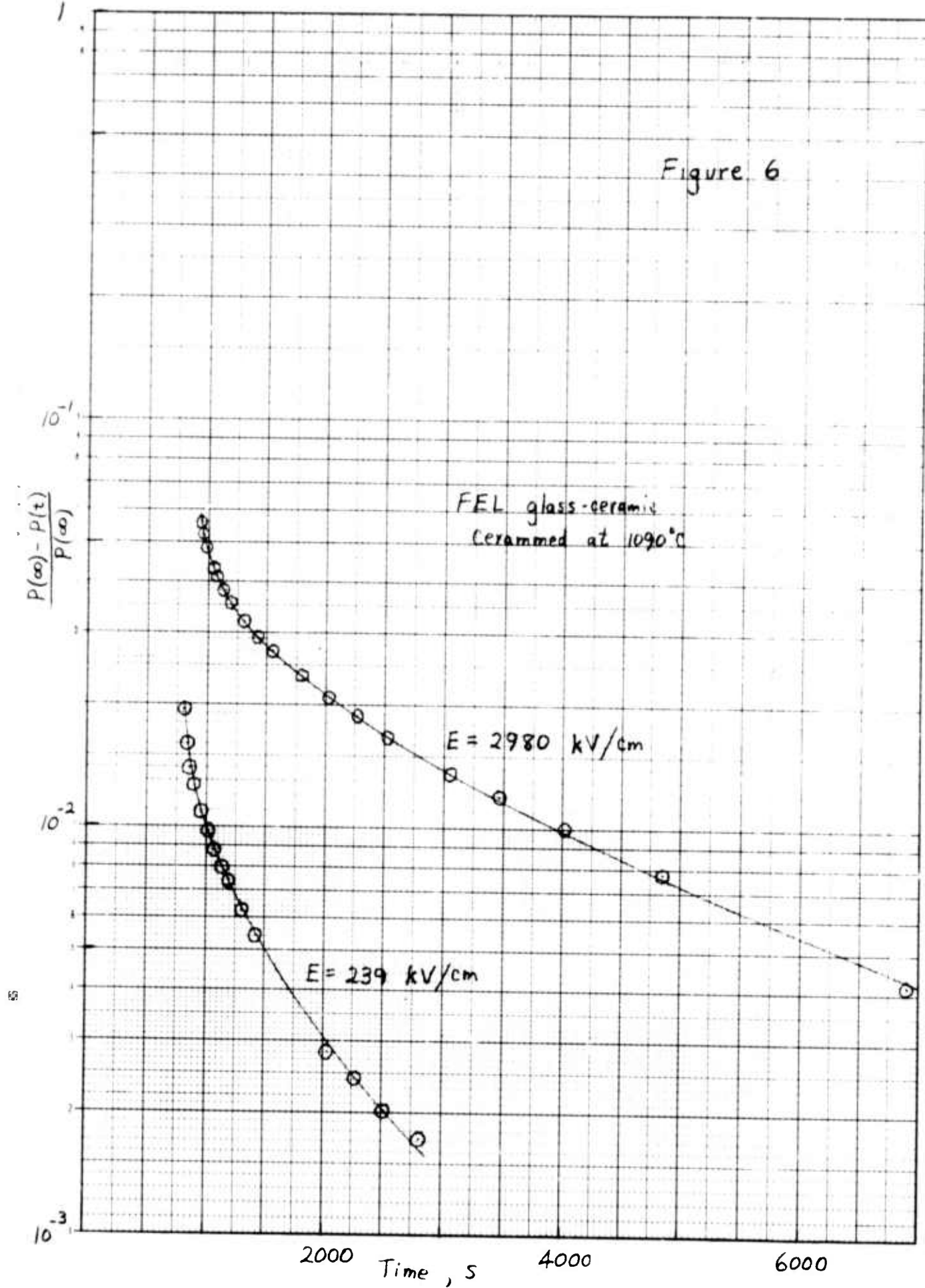


Figure 6



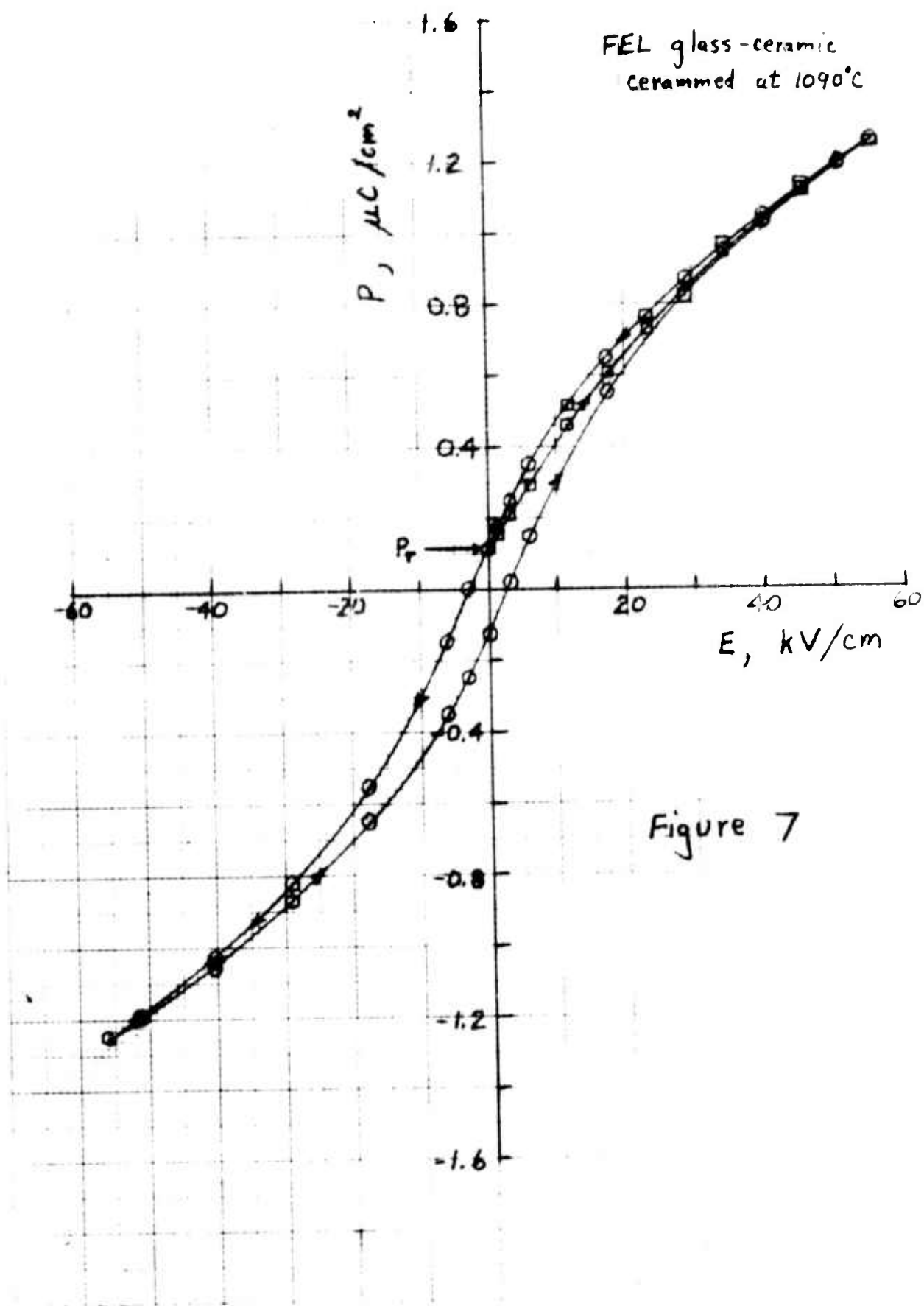


Figure 7

NORMALIZED POLARIZATION

